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(21) International Application Number: PCT/US91/00589 (22) International Filing Date: 28 January 1991 (28.01.91) (30) Priority data: 471,158 26 January 1990 (26.01.90) US (71) Applicant: CHEVRON RESEARCH AND TECHNOLOGY COMPANY [US/US]; Post Office Box 7141, San Francisco, CA 94120-7141 (US). (72) Inventors: ZONES, Stacey, I. ; 1874 9th Avenue, San Francisco, CA 94122 (US). HARRIS, Thomas, V. ; 183 W. Seaview Drive, Benicia, CA 94510 (US). RAINIS, Andrew ; 50 Hanson Lane, Walnut Creek, CA 94594 (US). SANTILLI, Donald, S. ; 260 Piedmont Road, Larkspur, CA 94939 (US).		(74) Agents: RINCON, Cathy, E. et al.; Chevron Corporation, Post Office Box 7141, San Francisco, CA 94120-7141 (US). (81) Designated States: AT (European patent), AU, BB, BE (European patent), BG, BR, CA, CH (European patent), DE (European patent), DK, DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), GR (European patent), HU, IT (European patent), JP, KP, KR, LK, LU (European patent), MC, MG, MW, NL (European patent), NO, RO, SD, SE (European patent), SU. Published <i>With international search report.</i>
(54) Title: NEW ZEOLITE SSZ-31 (57) Abstract A crystalline zeolite SSZ-31 is prepared by various methods using quaternary ammonium ion templates wherein the product zeolite has a mole ratio of an oxide selected from silicon oxide, germanium oxide and mixtures thereof to an oxide selected from aluminum oxide, gallium oxide, iron oxide, and mixtures thereof greater than about 50:1, and wherein said zeolite has a unique X-ray diffraction pattern.		

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NEW ZEOLITE SSZ-31

BACKGROUND OF THE INVENTION

01
02
03
04
05 Natural and synthetic zeolitic crystalline metalosilicates
06 are useful as catalysts and adsorbents. Metalosilicate
07 molecular sieves are zeolites with a silicate lattice
08 wherein a metal can be substituted into the tetrahedral
09 positions of the silicate framework. These metals include
10 aluminum, gallium iron and mixtures thereof. These metallo-
11 silicates have distinct crystal structures which are
12 demonstrated by X-ray diffraction. The crystal structure
13 defines cavities and pores which are characteristic of the
14 different species. The adsorptive and catalytic properties
15 of each crystalline metalosilicate are determined in part by
16 the dimensions of its pores and cavities. Thus, the utility
17 of a particular zeolite in a particular application depends
18 at least partly on its crystal structure.

19
20 Because of their unique molecular sieving characteristics,
21 as well as their catalytic properties, some crystalline
22 metalosilicates are especially useful in such applications
23 as gas drying and separation and hydrocarbon conversion.
24 Although many different crystalline aluminosilicates,
25 borosilicate and silicates have been disclosed, there is a
26 continuing need for new zeolites and silicates with
27 desirable properties for gas separation and drying,
28 hydrocarbon and chemical conversions, and other
29 applications.

30
31 Crystalline aluminosilicates are usually prepared from
32 aqueous reaction mixtures containing alkali or alkaline
33 earth metal oxides, silica, and alumina. "Nitrogenous
34 zeolites" have been prepared from reaction mixtures

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01 containing an organic templating agent, usually a nitrogen-
02 containing organic cation. By varying the synthesis
03 conditions and the composition of the reaction mixture,
04 different zeolites can be formed using the same templating
05 agent. Use of N,N,N-trimethyl cyclopentylammonium iodide in
06 the preparation of Zeolite SSZ-15 molecular sieve is dis-
07 closed in U.S. Patent No. 4,610,854; use of 1-azoniaspiro
08 [4.4] nonyl bromide and N,N,N-trimethyl neopentylammonium
09 iodide in the preparation of a molecular sieve termed
10 "Losod" is disclosed in Helv. Chim. Acta (1974); Vol. 57,
11 p. 1533 (W. Sieber and W. M. Meier); use of quinuclidinium
12 compounds to prepare a zeolite termed "NU-3" is disclosed in
13 European Patent Publication No. 40016; use of
14 1,4-di(1-azoniabicyclo[2.2.2.]octane) lower alkyl compounds
15 in the preparation of Zeolite SSZ-16 molecular sieve is
16 disclosed in U.S. Patent No. 4,508,837; use of
17 N,N,N-trialkyl-1-adamantamine in the preparation of Zeolite
18 SSZ-13 molecular sieve is disclosed in U.S. Patent No.
19 4,544,538, and for SSZ-24 in U.S. Patent No. 4,665,110.

20
21 Synthetic zeolitic crystalline borosilicates are useful as
22 catalysts. Methods for preparing high silica content zeo-
23 lites that contain framework boron are known and disclosed
24 in U.S. Patent No. 4,269,813. The amount of boron contained
25 in the zeolite may be made to vary by incorporating
26 different amounts of borate ion in the zeolite-forming
27 solution. In some instances, it is necessary to provide
28 boron as a pre-formed borosilicate.

29

30 The present invention relates to a novel family of stable
31 synthetic crystalline materials identified as SSZ-31 and
32 having a specified X-ray diffraction pattern, and also to
33 the preparation and use of such materials.

34

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SUMMARY OF THE INVENTION

01

02

03 We have prepared a family of crystalline metallosilicate
04 molecular sieves with unique properties, referred to herein
05 as "Zeolite SSZ-31" or simply "SSZ-31", and have found
06 highly effective methods for preparing SSZ-31.

07

08 Metallosilicate molecular sieves are zeolites with a
09 silicate lattice wherein a metal can be substituted into the
10 tetrahedral positions of the silicate framework. These
11 metals include aluminum, gallium, iron, boron, titanium and
12 mixtures thereof.

13

14 The zeolite has compositions as synthesized and in the
15 anhydrous state, in terms of oxides as follows: $(1.0 \text{ to } 5)Q_2O:(0.1 \text{ to } 2.0)M_2O:W_2O_3(\text{greater than } 50)YO_2$, wherein M is
16 an alkali metal cation, W is selected from boron, Y is
17 selected from silicon, germanium and mixtures thereof, and Q
18 is a cyclic quaternary ammonium ion; and $(0.1 \text{ to } 10)Q'_2O:(0.1 \text{ to } 5.0)M_2O:W'_2O_3(\text{greater than } 100)Y'O_2$, wherein
19 M is an alkali metal cation, W' is selected from aluminum,
20 gallium, iron, and mixtures thereof, Y' is selected from
21 silicon, germanium and mixtures thereof and Q' is a
22 tricyclodecane quaternary ammonium ion.

23

24 SSZ-31 zeolites may be prepared using various methods. The
25 method for preparing SSZ-31 with a $YO_2:W_2O_3$ mole ratio
26 greater than 50:1 comprises preparing an aqueous mixture
27 containing sources of a quaternary ammonium ion, an alkali
28 oxide, an oxide selected from boron as a borosilicate, not
29 simply a boron oxide, and an oxide selected from silicon
30 oxide, germanium oxide, and mixtures thereof, and having a
31 composition, in terms of mole ratios of oxides, falling
32 within the following ranges: YO_2/W_2O_3 , greater than 50:1;

33

34

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01 wherein Y is selected from silicon, germanium, and mixtures
02 thereof, W is selected from boron, and Q is a quaternary
03 ammonium ion; maintaining the mixture at a temperature of at
04 least 100°C until the crystals of said zeolite are formed;
05 and recovering said crystals.

06

07 A preferred borosilicate source is boron beta zeolite
08 described in commonly assigned co-pending application U.S.
09 Serial No. 377,359 filed July 7, 1989, and entitled
10 "Low-Aluminum Boron Beta Zeolite".

11

12 The method for preparing SSZ-31 with a $Y'O_2:W'_2O_3$ mole ratio
13 greater than 100:1 comprises preparing an aqueous mixture
14 containing sources of a tricyclodecane quaternary ammonium
15 ion, an oxide selected from aluminum oxide, gallium oxide,
16 iron oxide, and mixtures thereof, and an oxide selected from
17 silicon oxide, germanium oxide, and mixtures thereof, and
18 having a composition, in terms of mole ratios of oxides,
19 falling within the following ranges: $Y'O_2/W'_2O_3$, 100:1 to
20 infinity (essentially pure $Y'O_2$); wherein Y' is selected
21 from silicon, germanium, and mixtures thereof, W' is
22 selected from aluminum, gallium, iron, and mixtures thereof,
23 and Q' is a tricyclodecane quaternary ammonium ion;
24 maintaining the mixture at a temperature of at least 100°C
25 until the crystals of said zeolite are formed; and
26 recovering said crystals.

27

28 We have found that the SSZ-31 zeolite has unexpectedly
29 outstanding hydrocarbon conversion properties, particularly
30 including hydrocracking, chemicals production, reforming and
31 catalytic cracking.

32

33

34

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DETAILED DESCRIPTION OF THE INVENTION

SSZ-31 zeolites, as synthesized, have a crystalline structure whose X-ray powder diffraction pattern shows the following characteristic lines:

TABLE 1

<u>2 θ</u>	<u>d/n</u>	<u>I/I₀</u>
6.10	14.49	6
7.38	11.98	30
8.18	10.81	11
20.30	4.37	15
21.12	4.21	69
22.25	3.99	100
24.73	3.60	23
30.90	2.89	11

Typical SSZ-31 borosilicate zeolites have the X-ray diffraction patterns of Table 6 below.

The X-ray powder diffraction patterns were determined by standard techniques. The radiation was the K-alpha/doublet of copper and a scintillation counter spectrometer with a strip chart pen recorder was used. The peak heights I and the positions, as a function of 2 θ where θ is the Bragg angle, were read from the spectrometer chart. From these measured values, the relative intensities, $100I/I_0$, where I_0 is the intensity of the strongest line or peak, and d, the interplanar spacing in Angstroms corresponding to the recorded lines, can be calculated. The X-ray diffraction pattern of Table 1 is characteristic of SSZ-31 zeolites. The zeolite produced by exchanging the metal or other cations present in the zeolite with various other cations

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01 yields substantially the same diffraction pattern although
 02 there can be minor shifts in interplanar spacing and minor
 03 variations in relative intensity. Minor variations in the
 04 diffraction pattern can also result from variations in the
 05 organic compound used in the preparation and from variations
 06 in the silica-to-alumina mole ratio from sample to sample.
 07 Calcination can also cause minor shifts in the X-ray
 08 diffraction pattern. Notwithstanding these minor
 09 perturbations, the basic crystal lattice structure remains
 10 unchanged.

11

12 Various methods can be used to prepare the SSZ-31 zeolite.
 13 SSZ-31 zeolites with a $YO_2:W_2O_3$ mole ratio greater than 50:1
 14 can be suitably prepared from an aqueous solution containing
 15 sources of an alkali metal oxide, a quaternary ammonium ion,
 16 borosilicate, and an oxide of silicon or germanium, or
 17 mixture of the two. The reaction mixture should have a
 18 composition in terms of mole ratios falling within the
 19 following ranges:

20

21

22

23

24

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26

27

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31

32

33

34

	<u>Broad</u>	<u>Preferred</u>
YO_2/W_2O_3	30-∞	50-∞
OH/YO_2	0.10-0.50	0.15-0.25
Q/YO_2	0.05-0.50	0.10-0.25
$M+/YO_2$	0.05-0.30	0.05-0.15
H_2O/YO_2	15-300	25-60
$Q/Q+M+$	0.30-0.70	0.40-0.60

wherein Q is a quaternary ammonium ion, Y is silicon,
 germanium or both, and W is boron. M is an alkali metal,
 preferably sodium. The organic compound which acts as a

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01 source of the quaternary ammonium ion employed can provide
 02 hydroxide ion. W is shown as boron, but is provided to the
 03 reaction as borosilicate. The quaternary ammonium compounds
 04 which may be used to prepare these SSZ-31 zeolites are shown
 05 in Table 2 as Templates B-F. Examples 12, 13, 14, 15 and 16
 06 show methods of preparing the Templates B-F in Table 2.

07

08 When using the quaternary ammonium hydroxide compound as a
 09 template, it has also been found that purer forms of SSZ-31
 10 are prepared when there is an excess of compound present
 11 relative to the amount of alkali metal hydroxide.

12

13

TABLE 2

14

15

Organo-Cations Which Are

16

Representative of Directing Boron SSZ-31 Synthesis

17

18

Structure

19

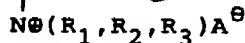
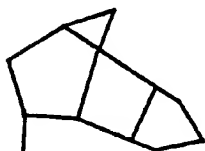
Template

20

21

22

23



24

A

25

N,N,N trimethylammonium-8-tricyclo[5.2.1.0]decane

26

27

28

29

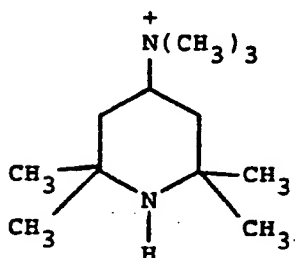
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B

4 trimethylammonium-2,2,6,6 tetramethyl piperidine

-8-

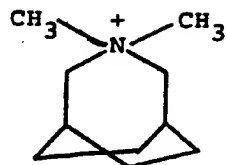
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05



C

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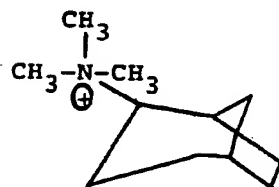
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D

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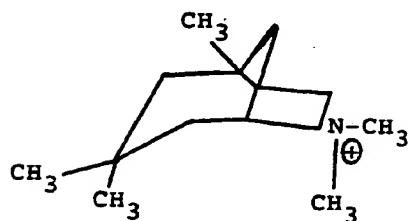
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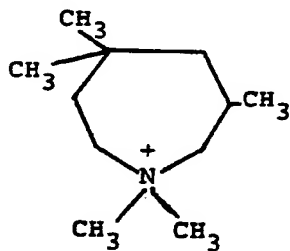
30

31

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34



F

N,N,3,5,5,pentamethyl azonium cycloheptane

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01 The reaction mixture is prepared using standard zeolitic
02 preparation techniques. Sources of borosilicates for the
03 reaction mixture include borosilicate glasses and most
04 particularly, other reactive borosilicate molecular sieves.
05 One very reactive source is boron beta zeolite described in
06 commonly assigned co-pending application U.S. Serial
07 No. 377,359, filed July 7, 1989, and entitled "Low-Aluminum
08 Boron Beta Zeolite". Typical sources of silicon oxide
09 include silicates, silica hydrogel, silicic acid, colloidal
10 silica, fumed silica, tetra-alkyl orthosilicates, and silica
11 hydroxides.

12
13 The reaction mixture is maintained at an elevated
14 temperature until the crystals of the zeolite are formed.
15 The temperatures during the hydrothermal crystallization
16 step are typically maintained from about 120°C to about
17 200°C, preferably from about 130°C to about 170°C and most
18 preferably from about 135°C to about 165°C. The
19 crystallization period is typically greater than one day and
20 preferably from about three days to about seven days.

21
22 The hydrothermal crystallization is conducted under pressure
23 and usually in an autoclave so that the reaction mixture is
24 subject to autogenous pressure. The reaction mixture can be
25 stirred during crystallization.

26
27 Once the zeolite crystals have formed, the solid product is
28 separated from the reaction mixture by standard mechanical
29 separation techniques such as filtration. The crystals are
30 water-washed and then dried, e.g., at 90°C to 150°C from 8
31 to 24 hours, to obtain the as synthesized, SSZ-31 zeolite
32 crystals. The drying step can be performed at atmospheric
33 or subatmospheric pressures.

34

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01 During the hydrothermal crystallization step, the SSZ-31
 02 crystals can be allowed to nucleate spontaneously from the
 03 reaction mixture. The reaction mixture can also be seeded
 04 with SSZ-31 crystals both to direct, and accelerate the
 05 crystallization, as well as to minimize the formation of
 06 undesired borosilicate contaminants.
 07
 08 SSZ-31 with a $Y'O_2:W'_2O_3$ mole ratio greater than 100:1 can
 09 can be suitably prepared from an aqueous solution containing
 10 sources of an alkali metal oxide, a tricyclodecane
 11 quaternary ammonium ion, an oxide of aluminum, gallium,
 12 iron, or mixtures thereof, and an oxide of silicon or
 13 germanium, or mixture of the two. The reaction mixture
 14 should have a composition in terms of mole ratios falling
 15 within the following ranges:

	<u>Broad</u>	<u>Preferred</u>
19 $Y'O_2/W'_2O_3$	100- ∞	200- ∞
20 $OH^-/Y'O_2$	0.10-0.60	0.20-0.50
21 $Q'/Y'O_2$	0.05-0.50	0.10-0.40
22 $M^+/Y'O_2$	0.05-0.30	0.05-0.15
23 $H_2O/Y'O_2$	10-300	25-60
24 $Q'/Q'+M^+$	0.30-0.80	0.40-0.75

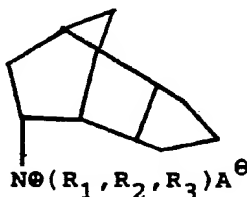
25
 26 wherein Q' is a tricyclodecane quaternary ammonium ion, Y'
 27 is silicon, germanium or both, and W' is aluminum, gallium,
 28 iron, or mixtures thereof. M is an alkali metal, preferably
 29 sodium or potassium. The organic tricyclodecane compound
 30 which acts as a source of the quaternary ammonium ion
 31 employed can provide hydroxide ion.

32
 33 When using the quaternary ammonium hydroxide compound as a
 34 template, it has also been found that purer forms of SSZ-31

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01 are prepared when there is an excess of tricyclodecane
 02 compound present relative to the amount of alkali metal
 03 hydroxide and that when the OH^-/SiO_2 molar ratio is greater
 04 than 0.40, then M^+/SiO_2 molar ratio should be less than
 05 0.20.

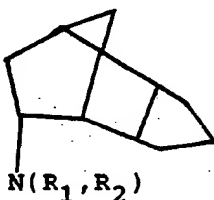
06
 07 The quaternary ammonium ion component Q, of the crystalli-
 08 zation mixture, is derived from a [5.2.1.0] tricyclodecane
 09 quaternary ammonium compound with the nitrogen at the eight
 10 position of the ring system. Preferably, the quaternary
 11 ammonium ion is derived from a compound of the Formula (1):



(1)

18
 19 wherein each of R_1 , R_2 and R_3 independently is lower alkyl
 20 and most preferably methyl; and A^- is an anion which is not
 21 detrimental to the formation of the zeolite. A method of
 22 making this template is described in Example 1.

23
 24 The tricyclodecane quaternary ammonium compounds of the
 25 Formula (1) above are prepared by methods known in the art.
 26 For example, compounds of the Formula (1) wherein A^- is a
 27 halide may be prepared by reacting an N,N-di(lower)alkyl-8-
 28 amino tricyclo [5.2.1.0] decane compound of the Formula (2):



(2)

-12-

01 wherein each of R_1 and R_2 independently is lower alkyl, with
02 a lower alkyl halide, in a solvent such as ethyl acetate.
03 The halide anion may be ion exchanged to obtain other anions
04 such as hydroxide, acetate, sulfate, carboxydate, and the
05 like. The N,N-di(lower)alkyl-8-amino tricycle [5.2.1.0]
06 decane of the Formula (2) above may be prepared by reacting
07 8-ketotricyclo [5.2.1.0] decane with a lower dialkyl
08 formamide in the presence of formic acid at a temperature in
09 the range of 160°-195°C in a closed system. The reaction
10 can be carried out for 10-50 hours, with the product
11 recovered by partitioning between ether and a basic aqueous
12 solution.

13
14 By "lower alkyl" is meant alkyl of from about 1 to 3 carbon
15 atoms.

16
17 A^\ominus is an anion which is not detrimental to the formation of
18 the zeolite. Representative of the anions include halogen,
19 e.g., fluoride, chloride, bromide and iodide, hydroxide,
20 acetate, sulfate, carboxylate, etc. Hydroxide is the most
21 preferred anion. It may be beneficial to ion-exchange, for
22 example, the halide for hydroxide ion, thereby reducing or
23 eliminating the alkali metal hydroxide quantity required.

24
25 The reaction mixture is prepared using standard zeolitic
26 preparation techniques. Typical sources of aluminum oxide
27 for the reaction mixture include aluminates, alumina, other
28 zeolites, and aluminum compounds such as $AlCl_3$ and
29 $Al_2(SO_4)_3$, and colloidal dispersions of alumina and alumina
30 on silica, such as the Nalco product 1SJ612. Typical
31 sources of silicon oxide include silicates, silica hydrogel,
32 silicic acid, colloidal silica, tetraalkyl orthosilicates,
33 and silica hydroxides. Gallium, iron, and germanium can be
34 added in forms corresponding to their aluminum and silicon

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01 counterparts. Salts, particularly alkali metal halides such
02 as sodium chloride, can be added to or formed in the
03 reaction mixture. They are disclosed in the literature as
04 aiding the crystallization of zeolites while preventing
05 silica occlusion in the lattice.

06
07 The reaction mixture is maintained at an elevated
08 temperature until the crystals of the zeolite are formed.
09 The temperatures during the hydrothermal crystallization
10 step are typically maintained from about 140°C to about
11 200°C, preferably from about 150°C to about 170°C, and most
12 preferably from about 155°C to about 165°C. The crystalli-
13 zation period is typically greater than 1 day and preferably
14 from about 6 days to about 12 days.

15
16 The hydrothermal crystallization is conducted under pressure
17 and usually in an autoclave so that the reaction mixture is
18 subject to autogenous pressure. The reaction mixture can be
19 stirred during crystallization.

20
21 Once the zeolite crystals have formed, the solid product is
22 separated from the reaction mixture by standard mechanical
23 separation techniques such as filtration. The crystals are
24 waterwashed and then dried, e.g., at 90°C to 150°C for from
25 8 to 24 hours, to obtain the as synthesized, SSZ-31 zeolite
26 crystals. The drying step can be performed at atmospheric
27 or subatmospheric pressures.

28
29 During the hydrothermal crystallization step, the SSZ-31
30 crystals can be allowed to nucleate spontaneously from the
31 reaction mixture. The reaction mixture can also be seeded
32 with SSZ-31 crystals both to direct, and accelerate the
33 crystallization, as well as to minimize the formation of
34 undesired aluminosilicate contaminants.

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01 The synthetic SSZ-31 zeolites can be used as synthesized or
02 can be thermally treated (calcined). Usually, it is
03 desirable to remove the alkali metal cation by ion exchange
04 and replace it with hydrogen, ammonium, or any desired metal
05 ion. The zeolite can be leached with chelating agents,
06 e.g., EDTA or dilute acid solutions, to increase the
07 silica:alumina mole ratio. The zeolite can also be steamed;
08 steaming helps stabilize the crystalline lattice to attack
09 from acids. The zeolite can be used in intimate combination
10 with hydrogenating components, such as tungsten, vanadium,
11 molybdenum, rhenium, nickel, cobalt, chromium, manganese, or
12 a noble metal, such as palladium or platinum, for those
13 applications in which a hydrogenation-dehydrogenation
14 function is desired. Typical replacing cations can include
15 metal cations, e.g., rare earth, Group IIA and Group VIII
16 metals, as well as their mixtures. Of the replacing
17 metallic cations, cations of metals such as rare earth, Mn,
18 Ca, Mg, Zn, Cd, Pt, Pd, Ni, Co, Ti, Al, Sn, Fe, and Co are
19 particularly preferred.

20
21 The hydrogen, ammonium, and metal components can be
22 exchanged into the zeolite. The zeolite can also be
23 impregnated with the metals, or, the metals can be
24 physically intimately admixed with the zeolite using
25 standard methods known to the art. And, some metals can be
26 occluded in the crystal lattice by having the desired metals
27 present as ions in the reaction mixture from which the
28 SSZ-31 zeolite is prepared.

29
30 Typical ion exchange techniques involve contacting the
31 synthetic zeolite with a solution containing a salt of the
32 desired replacing cation or cations. Although a wide
33 variety of salts can be employed, chlorides and other

34

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01 halides, nitrates, and sulfates are particularly preferred.
02 Representative ion exchange techniques are disclosed in a
03 wide variety of patents including U.S. Nos. 3,140,249;
04 3,140,251; and 3,140,253. Ion exchange can take place
05 either before or after the zeolite is calcined.

06
07 Following contact with the salt solution of the desired
08 replacing cation, the zeolite is typically washed with water
09 and dried at temperatures ranging from 65°C to about 315°C.
10 After washing, the zeolite can be calcined in air or inert
11 gas at temperatures ranging from about 200°C to 820°C for
12 periods of time ranging from 1 to 48 hours, or more, to
13 produce a catalytically active product especially useful in
14 hydrocarbon conversion processes.

15
16 Regardless of the cations present in the synthesized form of
17 the zeolite, the spatial arrangement of the atoms which form
18 the basic crystal lattice of the zeolite remains essentially
19 unchanged. The exchange of cations has little, if any,
20 effect on the zeolite lattice structures.

21
22 The SSZ-31 zeolites can be formed into a wide variety of
23 physical shapes. Generally speaking, the zeolite can be in
24 the form of a powder, a granule, or a molded product, such
25 as extrudate having particle size sufficient to pass through
26 a 2-mesh (Tyler) screen and be retained on a 400-mesh
27 (Tyler) screen. In cases where the catalyst is molded, such
28 as by extrusion with an organic binder, the aluminosilicate
29 can be extruded before drying, or, dried or partially dried
30 and then extruded. The zeolite can be composited with other
31 materials resistant to the temperatures and other conditions
32 employed in organic conversion processes. Such matrix
33 materials include active and inactive materials and
34 synthetic or naturally occurring zeolites as well as

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01 inorganic materials such as clays, silica and metal oxides.
02 The latter may occur naturally or may be in the form of
03 gelatinous precipitates, sols, or gels, including mixtures
04 of silica and metal oxides. Use of an active material in
05 conjunction with the synthetic zeolite, i.e., combined with
06 it, tends to improve the conversion and selectivity of the
07 catalyst in certain organic conversion processes. Inactive
08 materials can suitably serve as diluents to control the
09 amount of conversion in a given process so that products can
10 be obtained economically without using other means for
11 controlling the rate of reaction. Frequently, zeolite
12 materials have been incorporated into naturally occurring
13 clays, e.g., bentonite and kaolin. These materials, i.e.,
14 clays, oxides, etc., function, in part, as binders for the
15 catalyst. It is desirable to provide a catalyst having good
16 crush strength, because in petroleum refining the catalyst
17 is often subjected to rough handling. This tends to break
18 the catalyst down into powders which cause problems in
19 processing.

20
21 Naturally occurring clays which can be composited with the
22 synthetic zeolites of this invention include the
23 montmorillonite and kaolin families, which families include
24 the sub-bentonites and the kaolins commonly known as Dixie,
25 McNamee, Georgia, and Florida clays or others in which the
26 main mineral constituent is halloysite, kaolinite, dickite,
27 nacrite, or anauxite. Fibrous clays such as sepiolite and
28 attapulgite can also be used as supports. Such clays can be
29 used in the raw state as originally mined or can be
30 initially subjected to calcination, acid treatment or
31 chemical modification.

32

33

34

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01 In addition to the foregoing materials, the SSZ-31 zeolites
02 can be composited with porous matrix materials and mixtures
03 of matrix materials such as silica, alumina, titania,
04 magnesia, silica:alumina, silica-magnesia, silica-zirconia,
05 silica-thoria, silica-beryllia, silica-titania,
06 titania-zirconia as well as ternary compositions such as
07 silica-alumina-thoria, silica-alumina-zirconia,
08 silica-alumina-magnesia, and silica-magnesia-zirconia. The
09 matrix can be in the form of a cogel.

10
11 The SSZ-31 zeolites can also be composited with other
12 zeolites such as synthetic and natural faujasites (e.g., X
13 and Y), erionites, and mordenites. They can also be
14 composited with purely synthetic zeolites such as those of
15 the ZSM series. The combination of zeolites can also be
16 composited in a porous inorganic matrix.

17
18 SSZ-31 zeolites are useful in hydrocarbon conversion
19 reactions. Hydrocarbon conversion reactions are chemical
20 and catalytic processes in which carbon-containing compounds
21 are changed to different carbon-containing compounds.
22 Examples of hydrocarbon conversion reactions include
23 catalytic cracking, hydrocracking, and olefin and aromatics
24 formation reactions. The catalysts are useful in other
25 petroleum refining and hydrocarbon conversion reactions such
26 as isomerizing n-paraffins and naphthenes, polymerizing and
27 oligomerizing olefinic or acetylenic compounds such as
28 isobutylene and butene-1, reforming, alkylating, isomerizing
29 polyalkyl substituted aromatics (e.g., ortho xylene), and
30 disproportionating aromatics (e.g., toluene) to provide
31 mixtures of benzene, xylenes, and higher methylbenzenes.
32 The SSZ-31 catalysts have high selectivity, and under
33 hydrocarbon conversion conditions can provide a high
34 percentage of desired products relative to total products.

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01 SSZ-31 zeolites can be used in processing hydrocarbonaceous
02 feedstocks. Hydrocarbonaceous feedstocks contain carbon
03 compounds and can be from many different sources, such as
04 virgin petroleum fractions, recycle petroleum fractions,
05 shale oil, liquefied coal, tar sand oil, and in general, can
06 be any carbon containing fluid susceptible to zeolitic
07 catalytic reactions. Depending on the type of processing
08 the hydrocarbonaceous feed is to undergo, the feed can
09 contain metal or be free of metals, it can also have high or
10 low nitrogen or sulfur impurities. It can be appreciated,
11 however, that processing will generally be more efficient
12 (and the catalyst more active) if the metal, nitrogen, and
13 sulfur content of the feedstock is lower.

14
15 Using the SSZ-31 catalyst which contains aluminum framework
16 substitution and a hydrogenation promoter, heavy petroleum
17 residual feedstocks, cyclic stocks, and other hydrocracking
18 charge stocks can be hydrocracked at hydrocracking
19 conditions including a temperature in the range of from
20 175°C to 485°C, molar ratios of hydrogen to hydrocarbon
21 charge from 1 to 100, a pressure in the range of from 0.5 to
22 350 bar, and a liquid hourly space velocity (LHSV) in the
23 range of from 0.1 to 30.

24
25 Hydrocracking catalysts comprising SSZ-31 contain an
26 effective amount of at least one hydrogenation catalyst
27 (component) of the type commonly employed in hydrocracking
28 catalysts. The hydrogenation component is generally
29 selected from the group of hydrogenation catalysts
30 consisting of one or more metals of Group VIB and Group
31 VIII, including the salts, complexes, and solutions
32 containing such. The hydrogenation catalyst is preferably
33 selected from the group of metals, salts, and complexes
34 thereof of the group consisting of at least one of platinum,

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01 palladium, rhodium, iridium, and mixtures thereof or the
02 group consisting of at least one of nickel, molybdenum,
03 cobalt, tungsten, titanium, chromium, and mixtures thereof.
04 Reference to the catalytically active metal or metals is
05 intended to encompass such metal or metals in the elemental
06 state or in some form such as an oxide, sulfide, halide,
07 carboxylate, and the like.

08

09 A hydrogenation component is present in the hydrocracking
10 catalyst in an effective amount to provide the hydrogenation
11 function of the hydrocracking catalyst and preferably in the
12 range of from 0.05% to 25% by weight.

13

14 SSZ-31 may be used to dewax a variety of feedstocks ranging
15 from relatively light distillate fractions up to high
16 boiling stocks such as whole crude petroleum, reduced
17 crudes, vacuum tower residua, cycle oils, synthetic crudes
18 (e.g., shale oils, tar sand oil, etc.), gas oils, vacuum gas
19 oils, foots oils, and other heavy oils. The feedstock will
20 normally be a $C_{10}+$ feedstock generally boiling above about
21 350°F since lighter oils will usually be free of significant
22 quantities of waxy components. However, the process is
23 particularly useful with waxy distillate stocks such as
24 middle distillate stocks including gas oils, kerosenes, and
25 jet fuels, lubricating oil stocks, heating oils and other
26 distillate fractions whose pour point and viscosity need to
27 be maintained within certain specification limits.

28

29 Lubricating oil stocks will generally boil above 230°C
30 (450°F), more usually above 315°C (600°F). Hydrocracked
31 stocks are a convenient source of lubricating stocks of this
32 kind and also of other distillate fractions since they
33 normally contain significant amounts of waxy n-paraffins.
34 The feedstock of the present process will normally be a $C_{10}+$

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01 feedstock containing paraffins, olefins, naphthenes,
02 aromatics and heterocyclic compounds and with a substantial
03 proportion of higher molecular weight n-paraffins and
04 slightly branched paraffins which contribute to the waxy
05 nature of the feedstock.

06

07 The catalytic dewaxing conditions are dependent on large
08 measure on the feed used and upon the desired pour point.
09 Generally, the temperature will be between about 200°C and
10 about 475°C, preferably between about 250°C and about 450°C.
11 The pressure is typically between about 15 psig and about
12 3000 psig, preferably between about 200 psig and 3000 psig.
13 The liquid hourly space velocity (LHSV) preferably will be
14 from 0.1 to 20, preferably between about 0.2 and about 10.

15

16 Hydrogen is preferably present in the reaction zone during
17 the catalytic dewaxing process. The hydrogen to feed ratio
18 is typically between about 500 and about 30,000 SCF/bbl
19 (standard cubic feet per barrel), preferably about 1,000 to
20 about 20,000 SCF/bbl. Generally, hydrogen will be separated
21 from the product and recycled to the reaction zone.
22 Typical feedstocks include light gas-oil, heavy gas-oils, and
23 reduced crudes boiling about 350°F.

24

25 The SSZ-31 hydrodewaxing catalyst may optionally contain a
26 hydrogenation component of the type commonly employed in
27 dewaxing catalysts. The hydrogenation component may be
28 selected from the group of hydrogenation catalysts consist-
29 ing of one or more metals of Group VIB and Group VIII,
30 including the salts, complexes and solutions containing such
31 metals. The preferred hydrogenation catalyst is at least
32 one of the group of metals, salts, and complexes selected
33 from the group consisting of at least one of platinum,
34 palladium, rhodium, iridium, and mixtures thereof or at

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01 least one from the group consisting of nickel, molybdenum,
02 cobalt, tungsten, titanium, chromium, and mixtures thereof.
03 Reference to the catalytically active metal or metals is
04 intended to encompass such metal or metals in the elemental
05 state or in some form such as an oxide, sulfide, halide,
06 carboxylate, and the like.

07

08 The hydrogenation component of the hydrodewaxing catalyst is
09 present in an effective amount to provide an effective
10 hydrodewaxing catalyst preferably in the range of from about
11 0.05 to 5% by weight.

12

13 The SSZ-31 hydrodewaxing catalyst may be used alone or in
14 conjunction with intermediate-pore (or medium-pore)
15 molecular sieves. These intermediate-pore molecular sieves
16 are shape selective in that they have a pore size which
17 admits straight-chain n-paraffins either alone or with only
18 slightly branched-chain paraffins but which exclude more
19 highly branched materials and cycloaliphatics. Molecular
20 sieves such as ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23 and
21 SAPO-11 are suitable for this purpose.

22

23 The intermediate-pore molecular sieves may be combined with
24 the SSZ-31 or the isomerization dewaxing step using SSZ-31
25 may be followed by a separate selective dewaxing step using
26 the intermediate-pore molecular sieves.

27

28 The relative amounts of the SSZ-31 component and shape
29 selective intermediate-pore molecular sieve component, if
30 any, will depend at least in part, on the selected hydro-
31 carbon feedstock and on the desired product distribution to
32 be obtained therefrom, but in all instances an effective
33 amount of SSZ-31 is employed. When a shape selective
34 molecular sieve component is employed, the relative weight

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01 ratio of the shape selective molecular sieve to the SSZ-31
02 is generally between about 10:1 and about 1:500, desirably
03 between about 10:1 and about 1:200, preferably between about
04 2:1 and about 1:50, and most preferably is between about 1:1
05 and about 1:20.

06
07 SSZ-31 can be used to convert light straight run naphthas
08 and similar mixtures to highly aromatic mixtures. Thus,
09 normal and slightly branched chained hydrocarbons, prefer-
10 ably having a boiling range above about 40°C and less than
11 about 200°C, can be converted to products having a
12 substantial aromatics content by contacting the hydrocarbon
13 feed with the zeolite at a temperature in the range of from
14 about 400°C to 600°C, preferably 480°C to 550°C at pressures
15 ranging from atmospheric to 10 bar, and LHSV ranging from
16 0.1 to 15.

17
18 The conversion catalyst preferably contain a Group VIII
19 metal compound to have sufficient activity for commercial
20 use. By Group VIII metal compound as used herein is meant
21 the metal itself or a compound thereof. The Group VIII
22 noble metals and their compounds, platinum, palladium, and
23 iridium, or combinations thereof can be used. The most
24 preferred metal is platinum. The amount of Group VIII metal
25 present in the conversion catalyst should be within the
26 normal range of use in reforming catalysts, from about 0.05
27 to 2.0 wt. %, preferably 0.2 to 0.8 wt. %.

28
29 The zeolite/Group VIII metal conversion catalyst can be used
30 without a binder or matrix. The preferred inorganic matrix,
31 where one is used, is a silica-based binder such as
32 Cab-O-Sil or Ludox. Other matrices such as magnesia and
33 titania can be used. The preferred inorganic matrix is
34 nonacidic.

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01 It is critical to the selective production of aromatics in
02 useful quantities that the conversion catalyst be
03 substantially free of acidity, for example, by poisoning the
04 zeolite with a basic metal, e.g., alkali metal, compound.
05 The zeolite is usually prepared from mixtures containing
06 alkali metal hydroxides and thus, have alkali metal contents
07 of about 1-2 wt. %. These high levels of alkali metal,
08 usually sodium or potassium, are unacceptable for most
09 catalytic applications because they greatly deactivate the
10 catalyst for cracking reactions. Usually, the alkali metal
11 is removed to low levels by ion exchange with hydrogen or
12 ammonium ions. By alkali metal compound as used herein is
13 meant elemental or ionic alkali metals or their basic
14 compounds. Surprisingly, unless the zeolite itself is
15 substantially free of acidity, the basic compound is
16 required in the present process to direct the synthetic
17 reactions to aromatics production.

18
19 The amount of alkali metal necessary to render the zeolite
20 substantially free of acidity can be calculated using
21 standard techniques based on the aluminum, gallium or iron
22 content of the zeolite. If a zeolite free of alkali metal
23 is the starting material, alkali metal ions can be ion
24 exchanged into the zeolite to substantially eliminate the
25 acidity of the zeolite. An alkali metal content of about
26 100%, or greater, of the acid sites calculated on a molar
27 basis is sufficient.

28
29 Where the basic metal content is less than 100% of the acid
30 sites on a molar basis, the test described in U.S. Patent
31 No. 4,347,394 which patent is incorporated herein by
32 reference, can be used to determine if the zeolite is
33 substantially free of acidity.

34

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01 The preferred alkali metals are sodium, potassium, and
02 cesium. The zeolite itself can be substantially free of
03 acidity only at very high silica:alumina mole ratios; by
04 "zeolite consisting essentially of silica" is meant a
05 zeolite which is substantially free of acidity without base
06 poisoning.

07

08 Hydrocarbon cracking stocks can be catalytically cracked in
09 the absence of hydrogen using SSZ-31 at LHSV from 0.5 to 50,
10 temperatures from about 260°F to 1625°F and pressures from
11 subatmospheric to several hundred atmospheres, typically
12 from about atmospheric to about five atmospheres.

13

14 For this purpose, the SSZ-31 catalyst can be composited with
15 mixtures of inorganic oxide supports as well as traditional
16 cracking catalyst.

17

18 The catalyst may be employed in conjunction with traditional
19 cracking catalysts, e.g., any aluminosilicate heretofore
20 employed as a component in cracking catalysts.

21 Representative of the zeolitic aluminosilicates disclosed
22 heretofore as employable as component parts of cracking
23 catalysts are Zeolite Y (including steam stabilized
24 chemically modified, e.g., ultra-stable Y), Zeolite X,
25 Zeolite beta (U.S. Patent No. 3,308,069), Zeolite ZK-20
26 (U.S. Patent No. 3,445,727), Zeolite ZSM-3 (U.S. Patent No.
27 3,415,736), faujasite, LZ-10 (U.K. Patent 2,014,970, June 9,
28 1982), ZSM-5-Type Zeolites, e.g., ZSM-5, ZSM-11, ZSM-12,
29 ZSM-23, ZSM-35, ZSM-38, ZSM-48, crystalline silicates such
30 as silicalite (U.S. Patent No. 4,061,724), erionite,
31 mordenite, offretite, chabazite, FU-1-type zeolite, NU-type
32 zeolites, LZ-210-type zeolite and mixtures thereof.
33 Traditional cracking catalysts containing amounts of Na₂O
34 less than about one percent by weight are generally

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01 preferred. The relative amounts of the SSZ-31 component and
02 traditional cracking component, if any, will depend at least
03 in part, on the selected hydrocarbon feedstock and on the
04 desired product distribution to be obtained therefrom, but
05 in all instances, an effective amount of SSZ-31 is employed.
06 When a traditional cracking catalyst (TC) component is
07 employed, the relative weight ratio of the TC to the SSZ-31
08 is generally between about 1:10 and about 500:1, desirably
09 between about 1:10 and about 200:1, preferably between about
10 1:2 and about 50:1, and most preferably between about 1:1
11 and about 20:1.

12

13 The cracking catalysts are typically employed with an
14 inorganic oxide matrix component which may be any of the
15 inorganic oxide matrix components which have been employed
16 heretofore in the formulation of FCC catalysts including:
17 amorphous catalytic inorganic oxides, e.g., catalytically
18 active silica-aluminas, clays, silicas, aluminas,
19 silica-aluminas, silica-zirconias, silica-magnesias,
20 alumina-borias, alumina-titanias, and the like and mixtures
21 thereof. The traditional cracking component and SSZ-31 may
22 be mixed separately with the matrix component and then mixed
23 or the TC component and SSZ-31 may be mixed and then formed
24 with the matrix component.

25

26 The mixture of a traditional cracking catalyst and SSZ-31
27 may be carried out in any manner which results in the
28 coincident presence of such in contact with the crude oil
29 feedstock under catalytic cracking conditions. For example,
30 a catalyst may be employed containing the traditional
31 cracking catalyst and a SSZ-31 in single catalyst particles
32 or SSZ-31 with or without a matrix component may be added as
33 a discrete component to a traditional cracking catalyst.

34

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01 SSZ-31 can also be used to oligomerize straight and branched
02 chain olefins having from about 2-21 and preferably 2-5
03 carbon atoms. The oligomers which are the products of the
04 process are medium to heavy olefins which are useful for
05 both fuels, i.e., gasoline or a gasoline blending stock and
06 chemicals.

07

08 The oligomerization process comprises contacting the olefin
09 feedstock in the gaseous state phase with SSZ-31 at a
10 temperature of from about 450°F to about 1200°F, a WHSV of
11 from about 0.2 to about 50 and a hydrocarbon partial
12 pressure of from about 0.1 to about 50 atmospheres.

13

14 Also, temperatures below about 450°F may be used to
15 oligomerize the feedstock, when the feedstock is in the
16 liquid phase when contacting the zeolite catalyst. Thus,
17 when the olefin feedstock contacts the zeolite catalyst in
18 the liquid phase, temperatures of from about 50°F to about
19 450°F, and preferably from 80 to 400°F may be used and a
20 WHSV of from about 0.05 to 20 and preferably 0.1 to 10. It
21 will be appreciated that the pressures employed must be
22 sufficient to maintain the system in the liquid phase. As
23 is known in the art, the pressure will be a function of the
24 number of carbon atoms of the feed olefin and the
25 temperature. Suitable pressures include from about 0 psig
26 to about 3000 psig.

27

28 The zeolite can have the original cations associated
29 therewith replaced by a wide variety of other cations
30 according to techniques well known in the art. Typical
31 cations would include hydrogen, ammonium, and metal cations
32 including mixtures of the same. Of the replacing metallic
33 cations, particular preference is given to cations of metals
34 such as rare earth metals, manganese, calcium, as well as

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01 metals of Group II of the Periodic Table, e.g., zinc, and
02 Group VIII of the Periodic Table, e.g., nickel. One of the
03 prime requisites is that the zeolite have a fairly low
04 aromatization activity, i.e., in which the amount of
05 aromatics produced is not more than about 20 wt. %. This is
06 accomplished by using a zeolite with controlled acid
07 activity [alpha value] of from about 0.1 to about 120,
08 preferably from about 0.1 to about 100, as measured by its
09 ability to crack n-hexane.

10

11 Alpha values are defined by a standard test known in the
12 art, e.g., as shown in U.S. Patent No. 3,960,978 which is
13 incorporated herein by reference. If required, such
14 zeolites may be obtained by steaming, by use in a conversion
15 process or by any other method which may occur to one
16 skilled in this art.

17

18 SSZ-31 can be used to convert light gas C_2-C_6 paraffins
19 and/or olefins to higher molecular weight hydrocarbons
20 including aromatic compounds. Operating temperatures of
21 100-700°C, operating pressures of 0-1000 psig and space
22 velocities of 0.5-40 hr^{-1} WHSV can be used to convert the
23 C_2-C_6 paraffin and/or olefins to aromatic compounds.
24 Preferably, the zeolite will contain a catalyst metal or
25 metal oxide wherein said metal is selected from the group
26 consisting of Group IB, IIB, IIIA, or VIII of the Periodic
27 Table, and most preferably, gallium or zinc and in the range
28 of from about 0.05-5 wt. %.

29

30 SSZ-31 can be used to condense lower aliphatic alcohols
31 having 1-10 carbon atoms to a gasoline boiling point
32 hydrocarbon product comprising mixed aliphatic and aromatic
33 hydrocarbons. Preferred condensation reaction condition
34 using SSZ-31 as the condensation catalyst include a

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01 temperature of about 500-1000°F, a pressure of about
02 0.5-1000 psig and a space velocity of about 0.5-50 WHSV.
03 U.S. Patent No. 3,984,107 describes the condensation process
04 conditions in more detail. The disclosure of U.S. Patent
05 No. 3,984,107 is incorporated herein by reference.

06

07 The SSZ-31 catalyst may be in the hydrogen form or may be
08 base exchanged or impregnated to contain ammonium or a metal
09 cation complement, preferably in the range of from about
10 0.05-5 wt. %. The metal cations that may be present include
11 any of the metals of the Groups I-VIII of the Periodic
12 Table. However, in the case of Group IA metals, the cation
13 content should in no case be so large as to effectively
14 inactivate the catalyst.

15

16 The present SSZ-31 catalyst is highly active and highly
17 selective for isomerizing C₄ to C₇ hydrocarbons. The
18 activity means that the catalyst can operate at relatively
19 low temperatures which thermodynamically favors highly
20 branched paraffins. Consequently, the catalyst can produce
21 a high octane product. The high selectivity means that a
22 relatively high liquid yield can be achieved when the
23 catalyst is run at a high octane.

24

25 The isomerization process comprises contacting the
26 isomerization catalyst with a hydrocarbon feed under
27 isomerization conditions. The feed is preferably a light
28 straight run fraction, boiling within the range of 30-250°F
29 and preferably from 60-200°F. Preferably, the hydrocarbon
30 feed for the process comprises a substantial amount of C₄ to
31 C₇ normal and slightly branched low octane hydrocarbons,
32 more preferably C₅ and C₆ hydrocarbons.

33

34

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01 The pressure in the process is preferably between 50-1000
02 psig, more preferably between 100-500 psig. The LHSV is
03 preferably between about 1 to about 10 with a value in the
04 range of about 1 to about 4 being more preferred. It is
05 also preferable to carry out the isomerization reaction in
06 the presence of hydrogen. Preferably, hydrogen is added to
07 give a hydrogen to hydrocarbon ratio (H_2/HC) of between 0.5
08 and 10 H_2/HC , more preferably between 1 and 8 H_2/HC . The
09 temperature is preferably between about 200°F and about
10 1000°F, more preferably between 400-600°F. As is well known
11 to those skilled in the isomerization art, the initial
12 selection of the temperature within this broad range is made
13 primarily as a function of the desired conversion level
14 considering the characteristics of the feed and of the
15 catalyst. Thereafter, to provide a relatively constant
16 value for conversion, the temperature may have to be slowly
17 increased during the run to compensate for any deactivation
18 that occurs.

19
20 A low sulfur feed is especially preferred in the
21 isomerization process. The feed preferably contains less
22 than 10 ppm, more preferably less than 1 ppm, and most
23 preferably less than 0.1 ppm sulfur. In the case of a feed
24 which is not already low in sulfur, acceptable levels can be
25 reached by hydrogenating the feed in a presaturation zone
26 with a hydrogenating catalyst which is resistant to sulfur
27 poisoning. An example of a suitable catalyst for this
28 hydrosulfurization process is an alumina-containing
29 support and a minor catalytic proportion of molybdenum
30 oxide, cobalt oxide and/or nickel oxide. A platinum on
31 alumina hydrogenating catalyst can also work. In which
32 case, a sulfur sorber is preferably placed downstream of the
33 hydrogenating catalyst, but upstream of the present
34 isomerization catalyst. Examples of sulfur sorbers are

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01 alkali or alkaline earth metals on porous refractory
02 inorganic oxides, zinc, etc. Hydrodesulfurization is
03 typically conducted at 315-455°C, at 200-2000 psig, and at a
04 LHSV of 1-5.

05

06 It is preferable to limit the nitrogen level and the water
07 content of the feed. Catalysts and processes which are
08 suitable for these purposes are known to those skilled in
09 the art.

10

11 After a period of operation, the catalyst can become
12 deactivated by sulfur or coke. Sulfur and coke can be
13 removed by contacting the catalyst with an oxygen-containing
14 gas at an elevated temperature. If the Group VIII metal(s)
15 has agglomerated, then it can be redispersed by contacting
16 the catalyst with a chlorine gas under conditions effective
17 to redisperse the metal(s). The method of regenerating the
18 catalyst may depend on whether there is a fixed bed, moving
19 bed, or fluidized bed operation. Regeneration methods and
20 conditions are well known in the art.

21

22 The conversion catalyst preferably contains a Group VIII
23 metal compound to have sufficient activity for commercial
24 use. By Group VIII metal compound as used herein is meant
25 the metal itself or a compound thereof. The Group VIII
26 noble metals and their compounds, platinum, palladium, and
27 iridium, or combinations thereof can be used. Rhenium and
28 tin may also be used in conjunction with the noble metal.
29 The most preferred metal is platinum. The amount of Group
30 VIII metal present in the conversion catalyst should be
31 within the normal range of use in isomerizing catalysts,
32 from about 0.05-2.0 wt. %.

33

34

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01 SSZ-31 can be used in a process for the alkylation or
02 transalkylation of an aromatic hydrocarbon. The process
03 comprises contacting the aromatic hydrocarbon with a C_2 to
04 C_4 olefin alkylating agent or a polyalkyl aromatic
05 hydrocarbon transalkylating agent, under at least partial
06 liquid phase conditions, and in the presence of a catalyst
07 comprising SSZ-31.

08

09 For high catalytic activity, the SSZ-31 zeolite should be
10 predominantly in its hydrogen ion form. Generally, the
11 zeolite is converted to its hydrogen form by ammonium
12 exchange followed by calcination. If the zeolite is
13 synthesized with a high enough ratio of organonitrogen
14 cation to sodium ion, calcination alone may be sufficient.
15 It is preferred that, after calcination, at least 80% of the
16 cation sites are occupied by hydrogen ions and/or rare earth
17 ions.

18

19 The pure SSZ-31 zeolite may be used as a catalyst, but
20 generally, it is preferred to mix the zeolite powder with an
21 inorganic oxide binder such as alumina, silica,
22 silica-alumina, or naturally occurring clays and form the
23 mixture into tablets or extrudates. The final catalyst may
24 contain from 1-99 wt. % SSZ-31 zeolite. Usually the zeolite
25 content will range from 10-90 wt. %, and more typically from
26 60-80 wt. %. The preferred inorganic binder is alumina.
27 The mixture may be formed into tablets or extrudates having
28 the desired shape by methods well known in the art.

29

30 Examples of suitable aromatic hydrocarbon feedstocks which
31 may be alkylated or transalkylated by the process of the
32 invention include aromatic compounds such as benzene,
33

34

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01 toluene, and xylene. The preferred aromatic hydrocarbon is
02 benzene. Mixtures of aromatic hydrocarbons may also be
03 employed.

04

05 Suitable olefins for the alkylation of the aromatic
06 hydrocarbon are those containing 2-20 carbon atoms, such as
07 ethylene, propylene, butene-1, transbutene-2, and
08 cis-butene-2, or mixtures thereof. The preferred olefin is
09 propylene. These olefins may be present in admixture with
10 the corresponding C₂ to C₄ paraffins, but it is preferable
11 to remove any dienes, acetylenes, sulfur compounds or
12 nitrogen compounds which may be present in the olefin
13 feedstock stream to prevent rapid catalyst deactivation.

14

15 When transalkylation is desired, the transalkylating agent
16 is a polyalkyl aromatic hydrocarbon containing two or more
17 alkyl groups that each may have from two to about four
18 carbon atoms. For example, suitable polyalkyl aromatic
19 hydrocarbons include di-, tri-, and tetra-alkyl aromatic
20 hydrocarbons, such as diethylbenzene, triethylbenzene,
21 diethylmethylbenzene (diethyltoluene), di-isopropylbenzene,
22 di-isopropyltoluene, dibutylbenzene, and the like.
23 Preferred polyalkyl aromatic hydrocarbons are the dialkyl
24 benzenes. A particularly preferred polyalkyl aromatic
25 hydrocarbon is di-isopropylbenzene.

26

27 Reaction products which may be obtained include ethylbenzene
28 from the reaction of benzene with either ethylene or
29 polyethylbenzenes, cumene from the reaction of benzene with
30 propylene or polyisopropylbenzenes, ethyltoluene from the
31 reaction of toluene with ethylene or polyethyltoluenes,
32 cymenes from the reaction of toluene with propylene or
33 polyisopropyltoluenes, and secbutylbenzene from the reaction
34 of benzene and n-butenes or polybutylbenzenes. The

-33-

01 production of cumene from the alkylation of benzene with
02 propylene or the transalkylation of benzene with
03 di-isopropylbenzene is especially preferred.

04

05 When alkylation is the process conducted, reaction
06 conditions are as follows. The aromatic hydrocarbon feed
07 should be present in stoichiometric excess. It is preferred
08 that molar ratio of aromatics to olefins be greater than
09 four-to-one to prevent rapid catalyst fouling. The reaction
10 temperature may range from 100-600°F, preferably, 250-450°F.
11 The reaction pressure should be sufficient to maintain at
12 least a partial liquid phase in order to retard catalyst
13 fouling. This is typically 50-1000 psig depending on the
14 feedstock and reaction temperature. Contact time may range
15 from 10 seconds to 10 hours, but is usually from five
16 minutes to an hour. The WHSV, in terms of grams (pounds) of
17 aromatic hydrocarbon and olefin per gram (pound) of catalyst
18 per hour, is generally within the range of about 0.5 to 50.

19

20 When transalkylation is the process conducted, the molar
21 ratio of aromatic hydrocarbon will generally range from
22 about 1:1 to 25:1, and preferably from about 2:1 to 20:1.
23 The reaction temperature may range from about 100-600°F, but
24 it is preferably about 250-450°F. The reaction pressure
25 should be sufficient to maintain at least a partial liquid
26 phase, typically in the range of about 50-1000 psig,
27 preferably 300-600 psig. The WHSV will range from about
28 0.1-10.

29

30 The conversion of hydrocarbonaceous feeds can take place in
31 any convenient mode, for example, in fluidized bed, moving
32 bed, or fixed bed reactors depending on the types of process

33

34

-34-

01 desired. The formulation of the catalyst particles will
02 vary depending on the conversion process and method of
03 operation.

04
05 Other reactions which can be performed using the catalyst of
06 this invention containing a metal, e.g., platinum, include
07 hydrogenation-dehydrogenation reactions, denitrogenation,
08 and desulfurization reactions.

09
10 Some hydrocarbon conversions can be carried out on SSZ-31
11 zeolites utilizing the large pore shape-selective behavior.
12 For example, the substituted SSZ-31 zeolite may be used in
13 preparing cumene or other alkylbenzenes in processes
14 utilizing propylene to alkylate aromatics. Such a process
15 is described in our U.S. Serial No. 134,410 (1987), using
16 beta zeolite.

17
18 SSZ-31 can be used in hydrocarbon conversion reactions with
19 active or inactive supports, with organic or inorganic
20 binders, and with and without added metals. These reactions
21 are well known to the art, as are the reaction conditions.

22
23 SSZ-31 can also be used as an adsorbent, as a filler in
24 paper and paint, and as a water-softening agent in
25 detergents.

26
27 The following examples illustrate the preparation of SSZ-31.

28
29
30
31
32
33
34

-35-

EXAMPLESExample 1

Preparation of N,N,N-Trimethyl-8-Ammonium
Tricyclo[5.2.1.0] decane Hydroxide (Template A)

Five (5) grams of 8-ketotricyclo [5.2.1.0] decane (Aldrich Chemical Co.) was mixed with 2.63 gms of formic acid (88%) and 4.5 gms of dimethylformamide. The mixture was then heated in a pressure vessel for 16 hours at 190°C. Care should be taken to anticipate the increase in pressure the reaction experiences due to CO₂ evolution. The reaction was conveniently carried out in a Parr 4748 reactor with teflon liner. The workup consists of extracting N,N-dimethyl-8-amino tricyclo[5.2.1.0] decane from a basic (pH=12) aqueous solution with diethyl ether. The various extracts were dried with Na₂SO₄, the solvent removed and the product taken up in ethyl acetate. An excess of methyl iodide was added to a cooled solution which was then stirred at room temperature for several days. The crystals were collected and washed with diethyl ether to give N,N,N-trimethyl-8-ammonium tricyclo[5.2.1.0] decane iodide. The product has a melting point of 270-272°C and the elemental analyses and proton NMR are consistent with the expected structure. The vacuum-dried iodide salt was then ion-exchanged with ion-exchange resin AG 1x8 (in molar excess) to the hydroxide form. The exchange was performed over a column or more preferably by overnight stirring of the resin beads and the iodide salt in an aqueous solution designed to give about a 0.5 molar solution of the organic hydroxide. This is Template A (see Table 4).

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Example 2

01
02
03 1.5 Millimoles of the template from Example 1 were mixed
04 with 0.035 gm of NaOH (solid) in 7.5 ml H₂O. 0.60 Gram of
05 Cabosil M5 was stirred into the solution. The mixture was
06 heated in a Parr 4745 reactor at 150°C and without agitation
07 for 20 days. The contents of the reactor were filtered,
08 washed with distilled water, dried at 100°C and analyzed by
09 X-ray diffraction. The product was found to be the novel
10 structure SSZ-31. The pattern is tabulated in Table 3
11 below.

TABLE 3

	<u>2θ</u>	<u>d/n</u>	<u>I/I₀</u>
15			
16			
17	4.26	20.7	5
18	6.10	14.49	6
19	7.36	12.01	30
20	8.18	10.81	11
21	10.72	8.25	1
22	12.03	7.36	1
23	14.33	6.18	1
24	14.71	6.02	1
25	15.91	5.57	2
26	17.46	5.08	7
27	18.44	4.811	9
28	20.30	4.374	15
29	21.12	4.206	69
30	21.38	4.156	9
31	22.24	3.997	100
32	22.68	3.921	7
33	24.73	3.600	23
34	25.19	3.535	11
	25.70	3.466	5
	26.70	3.339	9
	27.20	3.278	5
	27.70	3.220	5
	28.18	3.167	2

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TABLE 3 (continued)

	<u>2θ</u>	<u>d/n</u>	<u>I/I₀</u>
01			
02			
03			
04			
05	28.77	3.103	4
06	29.00	3.079	3
07	29.50	3.028	2
08	29.82	2.996	5
09	30.56	2.925	2
10	30.90	2.894	11
11	32.16	2.783	5
12	32.76	2.734	6

Example 3

The same reaction mixture of Example 2 was formed again. A Parr 4745 reactor was used but this time it was loaded onto a rotating (30 rpm) spit of a Blue M oven which was rotated at 30 RPM. The tumbling reactors were heated at 160°C for 6 days. The analogous work-up and analysis produced a crystalline SSZ-31.

Example 4

2.25 Millimoles of template were mixed with 0.075 gm of NaOH (solid) and 12 ml of H₂O. 0.90 Gram of Cabosil were added and the reaction was run as in Example 3 except the Na/SiO₂ ratio had been increased. After 11 days of reaction, the product was mostly SSZ-31 but there was also some Kenyaitite and tridymite impurity.

Example 5

The same experiment as in Example 4 was repeated with the following few changes. NaOH was replaced by 0.09 gms of KOH (solid) and the reaction was run at 150°C and 0 RPM (no

-38-

01 stirring) and required 22 days to crystallize. The product
02 was SSZ-31 with a small amount of amorphous material.

03

04

Example 6

05

06 Example 5 was repeated. However, the reaction was seeded
07 with the product of Example 4. After 10 days at 160°C but
08 without stirring the product was SSZ-31 with a small
09 impurity of Kenyaitite. This run demonstrates that crys-
10 tallization, in the absence of stirring, can be made faster
11 by the use of seed crystals.

12

13

Example 7

14

15 (a) 5 Millimoles of the template of Example 1 and 0.06 gm
16 NaOH(s) were mixed in 11.8 mL H₂O. 0.90 Gram Cabosil was
17 stirred in to produce a homogeneous solution. 0.19 Gram of
18 Nalco 1SJ 612 (26% SiO₂, 4% Al₂O₃) was added with stirring
19 and several milligrams of seed crystals were also added.
20 The sealed reaction was carried out at 160°C, 39 rpm, and
21 over 10 days. The crystalline product was determined to be
22 a very broadlined version of SSZ-31.

23

24 (b) When the same reaction was run without seed crystals
25 and at 30 rpm, crystallization of SSZ-31 required 16 days.

26

27

Example 8

28

29 The same experiment as Example 7 was repeated, except the
30 source of aluminum was 0.05 gms Y zeolite (SK-40). Seeds of
31 SSZ-31 were once again added. After 10 days at 160°C and 30
32 rpm, the product had a broadlined version of SSZ-31 although
33 not as broadened as in Example 7.

34

-39-

Example 9

01

02

03 The crystalline products of Examples 2 and 4 were subjected
04 to calcination as follows. The samples were heated in a
05 muffle furnace from room temperature up to 540°C at a
06 steadily increasing rate over a 7-hour period. The samples
07 were maintained at 540°C for four more hours and then taken
08 up to 600°C for an additional four hours. A 50/50 mixture
09 of air and nitrogen was passed over the zeolite at a rate of
10 20 standard cubic feet per minute during heating. The cal-
11 cined product of Example 2 had the X-ray diffraction lines
12 indicated in Table 4 below.

13

14

TABLE 4

15

16

Calcined SSZ-31

17

18

19

20

21

22

23

24

25

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29

30

31

32

33

34

2 θ	d/n	100 x I/I ₀
5.05	17.5	2
6.10	14.49	27
7.39	11.96	96
8.19	10.80	43
10.35	8.55	1
10.81	8.18	6
12.20	7.25	2
14.45	6.13	14
14.84	5.97	9
16.00	5.54	1
17.54	5.06	5
18.46	4.806	6
20.37	4.360	13
21.10	4.210	64
21.53	4.127	4
22.40	3.969	100
23.78	3.742	1
24.85	3.583	14
25.20	3.534	4
26.20	3.401	14
26.80	3.326	6

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TABLE 4 (continued)

Calcined SSZ-31		
<u>2θ</u>	<u>d/n</u>	<u>100 x I/I₀</u>
27.70	3.220	2
28.20	3.164	1
28.95	3.084	3
29.18	3.060	3
29.83	2.995	3
30.00	2.979	3
31.00	2.885	7
32.32	2.770	3
32.86	2.726	3

Example 10

Ion-exchange of the calcined materials from Example 9 was carried out using NH_4NO_3 to convert the zeolites from Na form to NH_4 and then eventually to the H form. Typically, the same mass of NH_4NO_3 as zeolite was slurried into H_2O at ratio of 50/1 H_2O to zeolite. The exchange solution was heated at 100°C for two hours and then filtered. This process was repeated four times. Finally, after the last exchange, the zeolite was washed several times with H_2O and dried. A repeat calcination as in Example 9 was carried out but without the final treatment at 600°C . This produces the H form of the zeolites. The surface area for this material was $300 \text{ m}^2/\text{gm}$. The micro pore volume was 0.12 cc/gm as determined by the BET method with N_2 as absorbate.

Example 11

The product of Example 7(b) was treated as in Examples 9 and 10. Next, the zeolite powder was pelletized in a Carver press at 1000 psi. The pellets were broken up and meshed to

-41-

01 24-40 size. 0.35 Gram of the hydrogen form was loaded into
02 a 3/8-in. stainless steel tube with alumina packed on either
03 side of the bed. The bed was heated in a Lindberg furnace
04 and Helium (10 cc/min) was introduced into the reactor. The
05 catalyst was heated to 700°F. Once temperature equilibra-
06 tion was achieved, a 50/50 w/w feed of n-hexane/3 methyl-
07 pentane was introduced into the reactor at WHSV = 0.68. The
08 products were sampled on line by capillary G.C. At
09 10 minutes onstream, the conversion was 36% and indicated a
10 large pore zeolite.

11 Example 12

12
13
14 45 grams of 4-dimethylamino-2,2,6,6-tetramethyl piperidine
15 (Aldrich) is dissolved in 1.5 L of ethyl acetate. The
16 solution is chilled in an ice bath and 80 g of methyl iodide
17 is added dropwise with stirring. The reaction is allowed to
18 come to room temperature and is stirred for a few days. The
19 reaction is filtered. The solids are washed with
20 tetrahydrofuran and ether and then vacuum dried.

21
22 The crystalline salt is conveniently converted to the
23 hydroxide form by stirring overnight in water with AG1-X8
24 hydroxide ion exchange resin to achieve a solution ranging
25 from 0.25-1.5 molar. This is Template B (see Table 2).

26 Example 13

27
28
29 4 grams of 3 Azabicyclo [3.2.2] nonane is stirred into 100
30 ml of methanol. 3 grams of potassium bicarbonate are added
31 and the solution is chilled in an ice bath. Methyl iodide
32 (10 gms) is added dropwise and the solution is stirred for
33 15-25 hours. The inorganic solids are filtered off and the
34 methanol solution is stripped down. The residue is treated

-42-

01 with CHCl_3 which extracts the product. The clear CHCl_3
02 phase is now stripped down and the solid product is
03 recrystallized from a minimum of hot methanol. Subsequent
04 filtration, washing and ion-exchange is similar to Example
05 12. This is Template C (see Table 2).

06

07 Example 14

08

09 Template D (see Table 2) is prepared beginning with
10 bicyclo[3.2.1] octa-2-one. The reaction sequence and molar
11 ratios are the same as in Example 1.

12

13 Example 15

14

15 Template E (see Table 2) is prepared from 6-Aza, 1,3,3
16 Trimethyl-bicyclo[3.2.1] octane. The procedure and molar
17 ratios parallel Example 13.

18

19 Example 16

20

21 3,5,5, Trimethyl azacycloheptane is alkylated with methyl
22 iodide by the same procedure in Examples 13 and 15. The
23 crystalline product is Template F (see Table 2).

24

25 Example 17

26

27 2.25 millimoles of the hydroxide form of the template from
28 Example 12 and 0.09 g NaOH (solid) in a total of 12 mL H_2O
29 are stirred until clear. 0.90 g of NH_4^+ boron beta
30 (aluminum free and described in U.S. Serial No. 377,359) is
31 added and the reaction is heated at 160°C for six days and
32 at 30 rpm. The product after filtration and washing, drying
33 at 100°C , and XRD analysis is found to be SSZ-31 and some
34 quartz impurity. No remaining beta zeolite is observed.

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Example 18

The same experiment as Example 17 is set up except the NaOH is reduced to 0.06 g. Seeds of all silica SSZ-31 are added (20 mg). Heating is carried out at 150°C for six days, without stirring. The product is pure SSZ-31.

Examples 19-23

The following examples in Table 5 demonstrate the synthesis of SSZ-31 containing boron using templates B, C, D, E and F.

TABLE 5

Synthesis of Boron SSZ-31 Zeolite
(150°C, 4 days, 0 rpm)

Ex #	Template	mMoles as OH	1 N NaOH	H ₂ O*	NH ₄ Boron Beta	XRD
19	B	2.25	1.5	10.5	0.90 gms	SSZ-31
20	C	2.25	1.5	10.5	0.90 gms	SSZ-31
21	D	2.25	1.5	10.5	0.90 gms	SSZ-31
22	E	2.25	1.5	10.5	0.90 gms	SSZ-31
23	F	2.25	1.5	10.5	0.90 gms	SSZ-31

*Includes contribution from template solution and additional water added.

Example 24

The X-ray diffraction data for the uncalcined product from Example 22 is presented in Table 6. The uncalcined product of Example 22 was calcined as follows. The sample was

-44-

01 heated in a muffle furnace from room temperature up to 540°C
02 at a steadily increasing rate over a 7-hour period. The
03 sample was maintained at 540°C for four more hours and then
04 taken up to 600°C for an additional four hours. Nitrogen
05 was passed over the zeolite at a rate of 20 standard cfm
06 during heating. The calcined product had the X-ray
07 diffraction lines indicated in Table 7 below.

TABLE 6

X-Ray Diffraction Pattern for Uncalcined Product

2 θ	d/n	Intensity
6.08	14.54	17
7.35	12.03	17
8.00	11.05	12 (Broad)
16.00	5.54	2 (Broad)
17.40	5.10	5 (Broad)
18.48	4.80	19
20.35	4.36	16 (Broad)
21.11	4.21	180
22.24	4.00	100
22.62	3.93	10
24.71	3.60	38
25.60	3.48	3 (Broad)
26.70	3.34	3 (Broad)
30.88	2.90	12

-45-

TABLE 7

X-Ray Diffraction Pattern for Calcined Product

<u>2 θ</u>	<u>d/n</u>	<u>Intensity</u>
6.13	14.42	65
7.43	11.90	52
8.10	10.92	33
10.80	8.19	4 (Broad)
12.35	7.17	2 (Broad)
14.48	6.12	5
14.85	5.97	4
17.55	5.05	3 (Broad)
18.07	4.91	12
20.45	4.34	10
21.17	4.20	150
21.57	4.12	10
22.43	3.96	75
24.88	3.58	27
26.70	3.34	3 (Broad)
31.07	2.88	8

Example 25

Ion exchange of the calcined material from Example 17 was carried out using NH_4NO_3 to convert the zeolites from Na form to NH_4 . Typically the same mass of NH_4NO_3 as zeolite was slurried into H_2O at ratio of 50:1 H_2O :zeolite. The exchange solution was heated at 100°C for two hours and then filtered. This process was repeated two times. Finally,

-46-

01 after the last exchange, the zeolite was washed several
02 times with H₂O and dried.

03

04

Example 26

05

06

Constraint Index Determination

07

08 0.50 g of the hydrogen form of the zeolite of Example 17
09 (after treatment according to Examples 24 and 25) was packed
10 into a 3/8-inch stainless steel tube with alundum on both
11 sides of the zeolite bed. A lindburg furnace was used to
12 heat the reactor tube. Helium was introduced into the
13 reactor tube at 10 cc/minute and atmospheric pressure. The
14 reactor was taken to 250°F for 40 minutes and then raised to
15 800°F. Once temperature equilibration was achieved, a
16 50/50, w/w feed of n-hexane and 3-methylpentane was
17 introduced into the reactor at a rate of 0.62 cc/hour. Feed
18 delivery was made via syringe pump. Direct sampling onto a
19 gas chromatograph was begun after 10 minutes of feed
20 introduction. Constraint Index values were calculated from
21 gas chromatographic data using methods known in the art.

22

23

24

25

26

27

28

29

30 The product of Example 17 after treatment as in Examples 24
31 and 25 is refluxed overnight with Al(NO₃)₃·9H₂O with the
32 latter being the same mass as the zeolite and using the same
33 dilution as in the ion exchange of Example 25. The product
34 is filtered, washed, and calcined to 540°C. After

Synthesis Example No.	C.I.	Conversion at 10 Min.	Temp., °F
17	--	0	800

Example 27

-47-

01 pelletizing the zeolite powder and retaining the 20-40 mesh
02 fraction, the catalyst is tested as in Example 26. Data for
03 the reaction is given in Table 8.

TABLE 8

05
06
07 Constraint Index Determination
08 For Metal-Treated (B)SSZ-31

09	Synthesis	Metal		Conversion, %	Temp.,
10	Example	Salt	C.I.	(10 Min.)	°F
11	No.				
12	17	None	-	0	800
13	17	Al(NO ₃) ₃	0.89	34	700

14
15 Example 28

16
17 The all-silica version of SSZ-31 was evaluated as a
18 reforming catalyst. The zeolite powder was impregnated with
19 Pt(NH₃)₄·2NO₃ to give 0.7 wt. % Pt. The material was
20 calcined up to 600°F in air and maintained at this
21 temperature for three hours. The powder was pelletized on a
22 Carver press at 1000 psi and broken and meshed to 24-40.

23
24 The catalyst was evaluated at 950°F in hydrogen under the
25 following conditions:

26
27 psig = 200
28 H₂/HC = 6.4
29 WHSV = 6
30 Temp. = 950°F
31
32
33
34

-48-

01 The feed was an iC₇ mixture (Philips Petroleum Company):

02

03

04

05

06

07

08

09

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	Feed	Product 1.5 Hours Onstream, %
--	------	-------------------------------------

Conversion, %

36

Toluene

0.52

7.10

C₅-C₈ Octane

63.7

69.7

Example 29

The product of Example 7(a) was treated as in Examples 9 and 10. This catalyst now contained acidity due to aluminum incorporation. Two back ion-exchanges with KNO₃ were performed and the catalyst was calcined to 1000°F. Next, a reforming catalyst was prepared as in Example 28. The catalyst was evaluated under the following conditions:

psig = 200

H₂/HC = 6.4

WHSV = 6

Temp. = 800°F

The feed has an iC₇ mixture (Philips Petroleum Company).

The data for the run is given in Table 9. After 23 hours on stream, the temperature was raised to 900°F and this data also appears in the Table. By comparison with Example 28, the incorporation of aluminum into the zeolite gives a more active reforming catalyst.

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TABLE 9

01			
02			
03	Time	0.5 hrs.	1 hr (after 23
04			hrs.at 800°F)
05	Temp.	800°F	900°F
06	Conversion	19.4%	35.6%
07	Aromatization Select.	43.7%	55.6%
08	Toluene in Product	7.82%	18.93%
09	% Toluene in C ₅ + aromatics	92%	96%
10	C ₅ -C ₈ RON	67.2	72.7

Example 30

14 The product of Example 7(a) was treated as in Examples 9 and
15 10. Next, the catalyst was dried at 600°F, cooled in a
16 closed system and then vacuum impregnated with an aqueous
17 solution of Pd (NH₃)₄ 2 NO₃ to give 0.5 wt.% loading of
18 palladium. The catalyst was then calcined slowly up to
19 900°F in air and held there for three hours. Table 10 gives
20 run conditions and product data for the hydrocracking of
21 hexadecane. The catalyst is quite stable at the temper-
22 atures given.

TABLE 10

23			
24			
25			
26	Temp.	535°F	560°F
27	WHSV	1.55	1.55
28	PSIG	1200	1200
29	Conversion	94.2	99.8
30	Isom. select.	83.3	17.2
31	Crack. select.	16.7	82.9
32	C ₅ +C ₄	18	13.3
33	C ₅ +C ₆ /C ₅ +	13.2	17.9

34

-50-

01 The data shows that the catalyst has good isomerization
02 selectivity and that the liquid yield is high compared with
03 the gas make.

04

05

Example 31

06

07 The acid form of SSZ-31 was prepared as in Example 27 and
08 tested for the conversion of methanol to liquid products.
09 0.5 gm of catalyst was loaded into a 3/8-inch stainless
10 steel reactor tube which was heated in a Lindberg furnace to
11 1000°F. The temperature was reduced to 700°F in a stream of
12 helium at 20 cc/min. Methanol was introduced into the
13 reactor at a rate of 1.15 cc/hr. The conversion at 5
14 minutes was 100% and dropped over several hours. The
15 product distribution is given in Table 11 below.

16

17

TABLE 11

18

19

Conversion of Methanol over SSZ-31 Zeolite
(at 5 min.)

20

21

22

ProductWt. %

23

24

Methane

1.4

25

Ethylene

3.7

26

Ethane

0.2

27

Propylene

3.5

28

Propane

3.5

29

Isobutane

8.3

30

Methanol

<0.1

31

Dimethyl ether

0.0

32

1-Butene

0.7

33

n-Butane

1.5

34

1-Pentene

2.9

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TABLE 11 (continued)

Conversion of Methanol over SSZ-31 Zeolite
(at 5 min.)

<u>Product</u>	<u>Wt. %</u>
2-Methylpentane	0.7
Toluene	0.4
p-Xylene, m-Xylene	0.5
o-Xylene	<0.1
1,3,5-Trimethylbenzene	0.9
1,2,4-Trimethylbenzene	2.5%
1,2,3-Trimethylbenzene	0.5%
1,2,4,5-Tetramethylbenzene,	18.6%
1,2,3,5-Tetramethylbenzene	
1,2,3,4-Tetramethylbenzene	3.1%
Pentamethylbenzene	31.9
Hexamethylbenzene	5.3
Identified Peaks	86.5%
Unidentified Peaks	13.5%
(Greater than C ₆ or C ₇)	

Example 32

The boron version of SSZ-31 from Example 19 was evaluated as a reforming catalyst. The zeolite powder was impregnated with $\text{Pt}(\text{NH}_3)_4 \cdot 2\text{NO}_3$ to give 0.7 wt. % Pt. The material was calcined up to 600°F in air and maintained at this temperature for three hours. The powder was pelletized on a Carver press at 1000 psi and broken and meshed to 24-40.

-52-

01 The catalyst was evaluated at 800°F in hydrogen under the
02 following conditions:

03		Run 1	Run 2
04			
05	psig	200	50
06	H ₂ /HC	6.4	6.4
07	WHSV	6	6
08	Temp.	800°F	800°F
09	Time	23 hours	24 hours

10

11 The feed was an iC₇ mixture (Philips Petroleum Company).

12

13		Run 1	Run 2
14		Product	Product
15		%	%
16	Conversion, %	0	68.1
17	Aromatization Select.	0	39.4
18	Toluene	0.68	24.55
19	C ₅ -C ₈ RON	63.9	82.8

20

21

22

23

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01 WHAT IS CLAIMED IS:

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03 1. A zeolite having a mole ratio of an oxide selected from
04 silicon oxide, germanium oxide and mixtures thereof to
05 an oxide selected from aluminum oxide, gallium oxide,
06 iron oxide, and mixtures thereof greater than about
07 50:1, and having the X-ray diffraction lines of
08 Table 1.

09

10 2. A zeolite having a mole ratio of an oxide selected from
11 silicon oxide, germanium oxide, and mixtures thereof to
12 an oxide selected from boron oxide or mixtures of boron
13 oxide with aluminum oxide, gallium oxide, and iron
14 oxide, greater than 50:1, and having the X-ray
15 diffraction lines of Table 1.

16

17 3. A zeolite having a mole ratio of an oxide selected from
18 silicon oxide, germanium oxide, and mixtures thereof to
19 an oxide selected from boron oxide or mixtures of boron
20 oxide with aluminum oxide, greater than 50:1, and
21 having the X-ray diffraction lines of Table 1.

22

23 4. A zeolite having a mole ratio of silicon oxide to boron
24 oxide greater than 50:1 and having the X-ray
25 diffraction lines of Table 1.

26

27 5. A zeolite having a mole ratio of silicon oxide to
28 aluminum oxide greater than about 50:1 and having the
29 X-ray diffraction lines of Table 1.

30

31 6. A zeolite having a composition, as synthesized and in
32 the anhydrous state in terms of mole ratios of oxides
33 as follows:

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01 (0.1 to 10)Q₂O:(0.1 to 5.0)M₂O:W₂O₃(greater than 50)YO₂

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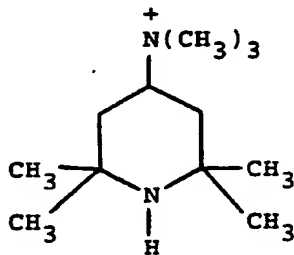
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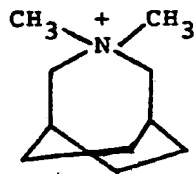
wherein M is an alkali metal cation, W is selected from boron, Y is selected from silicon, germanium, and mixtures thereof, Q is a quaternary ammonium ion and having the X-ray diffraction lines of Table 1.

7. A zeolite prepared by thermally treating the zeolite of Claim 6 at a temperature from about 200°C to 820°C.

8. A zeolite in accordance with Claim 6 wherein the quaternary ammonium ion is derived from a compound of the formula:

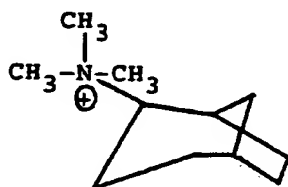


9. A zeolite in accordance with Claim 6 wherein the quaternary ammonium ion is derived from a compound of the formula:

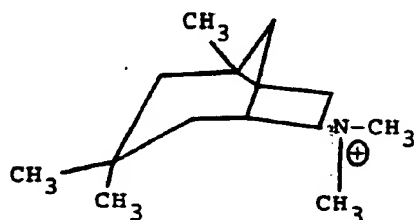


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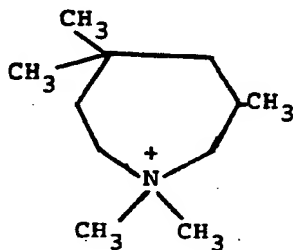
- 01 10. A zeolite in accordance with Claim 6 wherein the
02 quaternary ammonium ion is derived from a compound of
03 the formula:
04



- 11 11. A zeolite in accordance with Claim 6 wherein the
12 quaternary ammonium ion is derived from a compound of
13 the formula:
14



- 22 12. A zeolite in accordance with Claim 6 wherein the
23 quaternary ammonium ion is derived from a compound of
24 the formula:
25



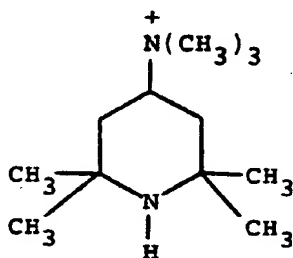
-56-

- 01 13. A zeolite in accordance with Claim 1, 2 or 3 which has
02 undergone ion exchange with hydrogen, ammonium, rare
03 earth metal, Group IIA metal, or Group VIII metal ions.
04
- 05 14. A zeolite in accordance with Claim 1, 2 or 3 wherein
06 rare earth metals, Group IIA metals, or Group VIII
07 metals are occluded in the zeolite.
08
- 09 15. A zeolite composition, comprising the zeolite of
10 Claim 1, 2 or 3 and an inorganic matrix.
11
- 12 16. A method for preparing the zeolite of Claim 2,
13 comprising:
14
- 15 (a) preparing an aqueous mixture containing sources of
16 a quaternary ammonium ion, an oxide selected from
17 boron oxide in a borosilicate form, and an oxide
18 selected from silicon oxide, germanium oxide, and
19 mixtures thereof;
20
- 21 (b) maintaining the mixture at a temperature of at
22 least 140°C until the crystals of said zeolite
23 form; and
24
- 25 (c) recovering said crystals.
26
- 27 17. A method in accordance with Claim 16 wherein the
28 borosilicate is borosilicate glass, or boron beta
29 zeolite.
30
- 31 18. The method in accordance with Claim 16 wherein the
32 aqueous mixture has a composition in terms of mole
33 ratios of oxides falling in the ranges: YO_2/W_2O_3 ,
34 greater than 50; Q/YO_2 , 0.05:1 to 0.50:1; wherein Y is

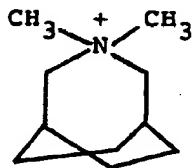
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01 selected from silicon, germanium, and mixtures thereof,
02 W is selected from boron and Q is a quaternary ammonium
03 compound.
04

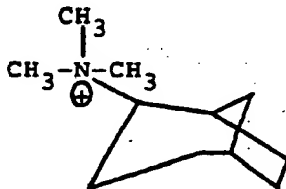
- 05 19. A method in accordance with Claims 16 and 17 wherein
06 the quaternary ammonium ion is derived from a compound
07 of the formula:
08



- 18 20. A method in accordance with Claims 16 and 17 wherein
19 the quaternary ammonium ion is derived from a compound
20 of the formula:
21

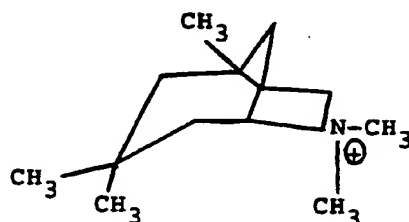


- 27 21. A method in accordance with Claims 16 and 17 wherein
28 the quaternary ammonium ion is derived from a compound
29 of the formula:
30

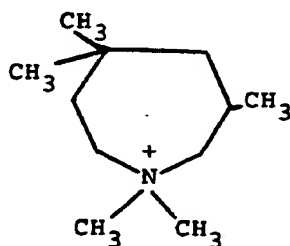


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- 01 22. A method in accordance with Claims 16 and 17 wherein
02 the quaternary ammonium ion is derived from a compound
03 of the formula:
04



- 13 23. A method in accordance with Claims 16 and 17 wherein
14 the quaternary ammonium ion is derived from a compound
15 of the formula:
16



- 25 24. A method for replacing the boron in the zeolite of
26 Claim 7 comprising contacting this boron-containing
27 zeolite with an aqueous solution of a Group IIIA metal
28 or a transition metal.
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01 25. A compound having the formula:

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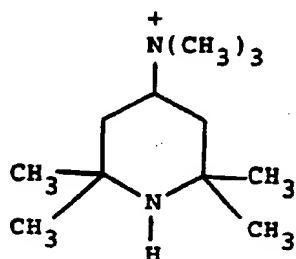
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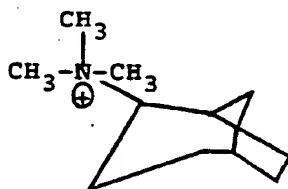
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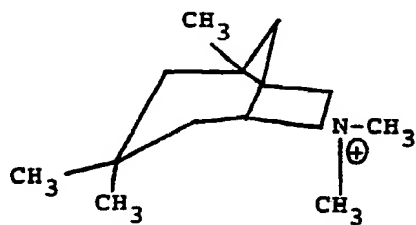
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26. A compound having the formula:



27. A compound having the formula:



28. A process for converting hydrocarbons comprising contacting a hydrocarbonaceous feed at hydrocarbon converting conditions with the zeolite of Claim 1.

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- 01 29. A process in accordance with Claim 28 which is a
02 hydrocracking process comprising contacting the
03 hydrocarbon feedstock under hydrocracking conditions
04 with the zeolite of Claim 1.
05
- 06 30. A process in accordance with Claim 28 which is a
07 process for preparing a high octane product having an
08 increased aromatics content comprising:
09
- 10 (a) contacting a hydrocarbonaceous feed, which com-
11 prises normal and slightly branched hydrocarbons
12 having a boiling range above about 40°C and less
13 than about 200°C under aromatic conversion con-
14 ditions with the zeolite of Claim 1, wherein said
15 zeolite is substantially free of acidity; and
16
- 17 (b) recovering a higher octane effluent.
18
- 19 31. A process in accordance with Claim 30 wherein the
20 zeolite contains a Group VIII metal component.
21
- 22 32. A process in accordance with Claim 28 which is a
23 hydrodewaxing process comprising contacting the
24 hydrocarbon feedstock under hydrodewaxing conditions
25 with the zeolite of Claim 1.
26
- 27 33. A process in accordance with Claim 28 which is a
28 catalytic cracking process comprising the step of
29 contacting the hydrocarbon feedstock in a reaction zone
30 under catalytic cracking conditions in the absence of
31 added hydrogen with a catalyst comprising the zeolite
32 of Claim 1.
33
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- 01 34. A process in accordance with Claim 33 which is a
02 catalytic cracking process comprising the step of
03 contacting the hydrocarbon feedstock in a reaction zone
04 under catalytic cracking conditions in the absence of
05 added hydrogen with a catalyst composition comprising a
06 component which is the zeolite of Claim 1 and a large
07 pore size crystalline aluminosilicate cracking
08 component.
09
- 10 35. A process in accordance with Claim 34 with a catalyst
11 composition comprising a component which is the zeolite
12 of Claim 1 and a large pore size crystalline
13 aluminosilicate cracking component.
14
- 15 36. A process as defined in Claim 35 wherein the
16 crystalline aluminosilicate cracking component has a
17 pore size greater than 7.0 angstroms.
18
- 19 37. A process in accordance with Claim 34 wherein the
20 catalyst compositions comprise a physical mixture of
21 the two components.
22
- 23 38. A process in accordance with Claim 34 wherein one of
24 the components is the zeolite of Claim 1 incorporated
25 in an inorganic oxide such as silica, alumina,
26 amorphous silica-alumina, silica-magnesia, silica
27 zirconia, alumina-boria, alumina-titanate, a synthetic
28 clay such as synthetic mica-montmorillonite, natural
29 clays such as kaolin, halloysite, montmorillonite,
30 attapulgite, sepiolite, and saponite, acid activated
31 clays, pillared or cross-linked clays, and mixtures
32 thereof.
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- 01 39. A process in accordance with Claim 34 wherein the two
02 catalyst components are incorporated in an inorganic
03 matrix comprised of the inorganic oxide of Claim 35.
04
- 05 40. A process in accordance with Claim 28 which is an
06 isomerizing process for isomerizing C_4 to C_7
07 hydrocarbons, comprising contacting a catalyst,
08 comprising at least one Group VIII metal and the
09 zeolite of Claim 1, with a feed having normal and
10 slightly branched C_4 to C_7 hydrocarbons under
11 isomerization conditions.
12
- 13 41. A process in accordance with Claim 40 wherein the
14 catalyst has been calcined in a steam/air mixture at an
15 elevated temperature after impregnation of the Group
16 VIII metal.
17
- 18 42. A process in accordance with Claim 40 wherein Group
19 VIII metal is platinum.
20
- 21 43. A process in accordance with Claim 28 which is a
22 process for alkylating an aromatic hydrocarbon which
23 comprises contacting under alkylating conditions at
24 least a mole excess of an aromatic hydrocarbon with a
25 C_2 to C_{20} olefin under at least partial liquid phase
26 conditions and in the presence of a zeolite according
27 to Claim 1.
28
- 29 44. A process in accordance with Claim 43 wherein the
30 aromatic hydrocarbon and olefin are present in a molar
31 ratio of about 4:1 to 20:1, respectively.
32
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- 01 45. A process in accordance with Claim 43 wherein the
02 aromatic hydrocarbon is a member selected from the
03 group consisting of benzene, toluene and xylene, or
04 mixtures thereof.
05
- 06 46. A process in accordance with Claim 28 which is a
07 process for transalkylating an aromatic hydrocarbon
08 which comprises contacting under transalkylating
09 conditions an aromatic hydrocarbon with a polyalkyl
10 aromatic hydrocarbon under at least partial liquid
11 phase conditions and in the presence of a zeolite
12 according to Claim 1.
13
- 14 47. A process in accordance with Claim 46 wherein said
15 aromatic hydrocarbon and said polyalkyl aromatic
16 hydrocarbon are present in a molar ratio of about 1:1
17 to about 25:1, respectively.
18
- 19 48. A process in accordance with Claim 46 wherein the
20 aromatic hydrocarbon is a member selected from the
21 group consisting of benzene, toluene and xylene, or
22 mixtures thereof.
23
- 24 49. A process in accordance with Claim 46 wherein the
25 polyalkyl aromatic hydrocarbon is dialkylbenzene.
26
- 27 50. A process in accordance with Claim 28 which is an
28 oligomerization process comprising contacting an olefin
29 feed under oligomerization conditions with the zeolite
30 of Claim 1.
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- 01 51. A process in accordance with Claim 28 which is a
02 catalytic reforming process comprising contacting a
03 hydrocarbonaceous feedstream under catalytic reforming
04 conditions with the zeolite of Claim 1.
05
- 06 52. A process in accordance with Claim 28 which is a
07 process for preparing a product having an increased
08 aromatic content comprising:
09
- 10 (a) contacting a hydrocarbonaceous feed, which
11 comprises normal and slightly branched
12 hydrocarbons having a boiling range above about
13 40°C and less than about 200°C under aromatic
14 conversion conditions with the zeolite of Claim 1
15 wherein said zeolite is substantially free of
16 acidity; and
17
- 18 (b) recovering an aromatic-containing effluent.
19
- 20 53. A process in accordance with Claim 28 for the catalytic
21 conversion of lower aliphatic alcohols having 1 to 8
22 carbon atoms to form gasoline boiling range
23 hydrocarbons which comprises contacting the alcohols
24 under converting conditions with a zeolite of Claim 1.
25
- 26 54. The process of Claim 53 wherein the alcohol is
27 methanol.
28
- 29 55. The process in accordance with Claim 28 which is a
30 process for converting a C₂-C₆ olefin or paraffin
31 feedstream to aromatic compounds comprising contacting
32 the feed material under aromatic conversion conditions
33 with a zeolite of Claim 1.
34

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US91/00589

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *

According to International Patent Classification (IPC) or to both National Classification and IPC
 IPC (5): B01J 29/04; C07C 45/34; C10G 11/05, 47/16
 U.S. Cl.: 502/64; 208/46, 111, 120; 568/360; 423/277, 329

II. FIELDS SEARCHED

Classification System

Minimum Documentation Searched ?

U.S.

502/64
 208/46, 111, 120
 568/260 and 423/277, 329

Classification Symbols

Documentation Searched other than Minimum Documentation
 to the extent that such Documents are included in the Fields Searched *

III. DOCUMENTS CONSIDERED TO BE RELEVANT *

Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US, A, 4,393,244 (BHADIRI ET AL), 12 July 1983, See entire document.	8-12, 19-27
A	US, A, 4,665,110 (ZONES), 12 May 1987, See entire document.	1-55
Y,P	US, A, 4,902,844 (ZONES ET AL) 20 February 1990, See entire document.	1-55
Y,P	US, A, 4,910,006 (ZONES, ET AL), 20 March 1990, See entire document.	1-55

* Special categories of cited documents: ¹⁰

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"A" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

12 March 1991

International Searching Authority

ISA/US

Date of Mailing of this International Search Report

16 MAY 1991

Signature of Authorized Officer

Anthony McFarlane